High Performance Oxide and Polymer Nanostructures for Advanced Solid-State Chemical Microsensors

Research underway at NIST, and through university collaborations, is aimed at developing nanoparticles, nanofibers, nanowires, nanotubes, and related structures of oxides and polymers for use in microsensor arrays and in microanalytical systems to increase sensitivity, selectivity, speed, and stability of chemical detection and monitoring. These nanomaterials are being studied as signal transducers for chemical sensing and as elements for upstream filtering and preconcentration of analytes. We focus on using individual structures as well as assembled hierarchical structures for chemical sensing applications where high-performance characteristics (such as nmol/mol sensitivity) are required. These well-defined nanostructures increase the surface area and active interfacial sites for adsorption and reaction of gas-phase analytes, thereby leading to more sensitive chemical measurements. These structures also enhance diffusion of the target molecules to functional sites by introduction of various scales of macro- and mesoporosity.

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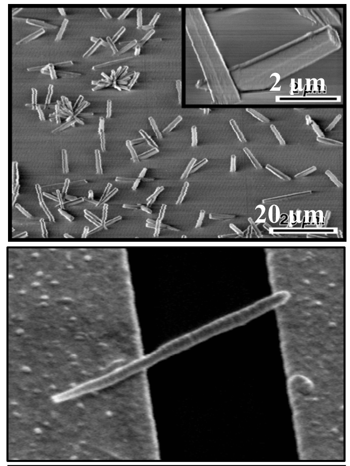
Specific materials being synthesized and studied include SnO_2 micro-shells, ultrathin layered oxides, pure and doped SnO_2 sol-gels, nanowire WO_3, nanorod ZnO, nanofiber polyaniline, and porous SiO_2. The SnO_2 micro-shells (which have undergone the most performance testing to date) are formed via a solution phase, layer-by-layer deposition of SnO_2 nanoparticles on sacrificial polystyrene spheres. These solutions are deposited on microhotplate platforms and the polystyrene spheres are removed by rapid heating to produce hollow, microporous SnO_2 shells with ultrathin walls. Films of these structures generally show sensitivities that are 5 to 10 times higher than more compact nanostructured films. Recent studies have demonstrated a rather complex dependence of sensitivity on the shell diameter, shell thickness, and film thickness. Related studies on ultrathin forms of TiO_2/SnO_2 and RuO_2/TiO_2 formed by chemical vapor deposition have shown that mixed materials generate responses that can be significantly different than either of the individual components. Initial evaluations of sol-gel SnO_2 deposited by dip pen nanolithography (DPN, collaboration with Northwestern) have indicated that platform/electrode modifications are necessary; these are being designed now to optimize responses from the DPN line geometries. Two new high-aspect-ratio-oxide nanostructures have been synthesized for gas sensing evaluation. ZnO crystalline nanorods, as shown in the SEM micrograph in the top figure, have been grown by hydrolysis of Zn(II) salts, and methods for controlling their nucleation density on substrates have been demonstrated. Porous polycarbonate membranes (100-nm pores) have been used as templates for the electrodepostion of WO_3 nanowires from $W_2O_{11}^{2-}$ in isopropanol solutions. Single wires have been isolated and positioned on electrode structures. The bottom figure is an SEM micrograph of a single WO_3 nanowire positioned on the electrodes of a microsensor device. Response studies on such isolated nanowires will allow us to perform comparative scaling studies as individual structures are assembled into larger networks and arrays. Porous silica is being developed as a high-area support material that can be functionalized to yield sorbent and reactive media for microscale preconcentrators and filters. Highly porous SiO_2 has been fabricated by heating silsesquioxane/block copolymer blends on microhotplate array elements. Conducting polymers are also being investigated to expand the range of analytes that can be sensed by multielement microarrays. Polyaniline nanofibers respond nearly 10 times faster than denser polyaniline films. Electrophoretic methods have been proven as a practical means for depositing the nanostructured polymers on microdevices.



SEM Micrographs of ZnO nanorods (top) and WO_3 nanowire (bottom)

Higher sensitivity, stability, speed, and reproducibility of sensing materials are critical to next-generation sensing devices.

These improved performance characteristics, attained by proper assembly of nano-building blocks, are expected to impact many application areas including alarm triggers for counter-terrorism, trace gas detection in space exploration, and the monitoring of gaseous biologically-generated compounds for medical diagnostics. Future studies at NIST and at collaborating institutions will develop more reproducible processing methods and explore both size effects and the fundamental mechanisms responsible for sensing enhancements realized through nano-engineering. Methods of manipulating and contacting nanostructures, particularly single particles, wires, and tubes, on microdevices will be refined.